

Sealing off a carbon nanotube with a self-assembled aqueous valve for the storage of hydrogen in GPa pressure

H.Y. Chen^{1,3}, D.Y. Sun¹, X.G. Gong,² and Zhi-Feng Liu^{3*}

¹Department of Physics

East China Normal University, Shanghai 200062, China

and

²Surface Physics Laboratory and Department of Physics

Fudan University, Shanghai 200433, China

and

³Department of Chemistry and

Centre for Scientific Modeling and Computation

Chinese University of Hong Kong

Shatin, Hong Kong, China

Abstract:

The end section of a carbon nanotube, cut by acid treatment, contains hydrophilic oxygen groups. Water molecules can self-assemble around these groups to seal off a carbon nanotube and form an “aqueous valve”. Molecular dynamics simulations on single-wall (12,12) and (15,15) tubes with dangling carboxyl groups show that the formation of aqueous valves can be achieved both in the absence of and in the presence of high pressure hydrogen. Furthermore, significant diffusion barriers through aqueous valves are identified. It indicates that such valves could hold hydrogen inside the tube with GPa pressure. Releasing hydrogen is easily achieved by melting the “aqueous valve”. Such a design provides a recyclable and non-destructive way to store hydrogen in GPa pressure. Under the storage conditions dictated by sealing off the container in liquid water, the hydrogen density inside the container is higher than that for solid hydrogen, which promises excellent weight storage efficiency.

*corresponding authors. email: zfliu@cuhk.edu.hk

As cylinders formed by rolling up robust graphenes, carbon nanotubes enclose much empty spaces. Foreign particles, including both ions and molecules, can be inserted into these tubes, to form quasi-1D structures with interesting physical and chemical properties. [1–3] Inserting hydrogen molecules into carbon nanotubes can be easily achieved, due to their small size. But for hydrogen, it is the compressibility, rather than the structure, that is the most interesting, [4–9] since H_2 has a weak van der Waals potential and is highly compressible all the way up to and above GPa pressure (tens of thousands of bars). [10,11] The mechanical strength of a carbon nanotube could stand pressure up to 40 GPa, as measured by experiment. [12] Therefore, compressing hydrogen to GPa pressure, which is two orders of magnitude higher than the pressure in a typical gas tank, would be ideal for the storage of hydrogen, provided a suitable nano-scale valve could be made. [4–6,9] Such a valve should block hydrogen inside carbon nanotubes, and control the filling and release of hydrogen in a recyclable and non-destructive way, which is a challenge in both design and implementation.

Attempts have been made to design such a nano valve. Our groups have suggested a design modeled after the "ball check valve", composed of a C_{60} molecule enclosed by a half-spherical carbon nanotube cap. Molecular dynamics (MD) simulations indicated that the position of C_{60} could be switched between "open" and "close" states, as the external pressure was varied. [4,6] Vakhrushev and Suyetin suggested that a positively charged endohedral complex $K^+@C_{60}$ could be used as the blocker for the storage of hydrogen and methane, which could then be controlled by the application of electric field. [9,13] Transition metal particles are often attached to the end of carbon nanotubes during the growth process, and asymmetric permeability of hydrogen through metal layers could also offer opportunities in designing a nano valve. [14] However, turning such elaborate designs into actual structures at the molecular level would be quite challenging. In this paper, we present a new design based on readily made structures that could be easily implemented.

Our starting point is the common structural feature of a carbon nanotube, typically consisted of two parts: a cylindrical tube body, which nowadays could be made into considerable length with little defects, and two end sections, where the caps are usually cut off by acid treatment and the dangling bonds are typically saturated by oxygen containing groups, such

as carboxyl(-COOH), carbonyl (-C=O) or hydroxy groups(-OH). [15,16] As curved graphene sheet, the tube wall contains no polar groups, and would prefer to bind non-polar molecules such as hydrogen. In contrast, the oxygen containing groups at the end sections are polar, and would prefer to bind with water molecules through hydrogen bonds.

Our design for the valve is to seal the open end section by exposure to water molecules. Around oxygen containing hydrophilic groups, water molecules should automatically aggregate to form an “aqueous valve”, hold together by hydrogen bonds. There must be a barrier for the diffusion of hydrogen through an aqueous valve. Filling hydrogen into the tube would require the growth of an aqueous valve in the presence of hydrogen under high pressure, while the diffusion barrier should lock the hydrogen inside after the withdrawal of external pressure. Experimental implementation of such a valve is straightforward, as it depends on the self-assembly of water molecules around the hydrophilic groups. Furthermore, nor is it difficult to modify these groups so that their structures and hydrophilic propensities could be adjusted. The crucial questions are therefore to examine the growth of the aqueous valve and to understand the mechanism and barrier for hydrogen diffusion through such a valve at various pressures.

Although the energy of one hydrogen bond between two water molecules is only around 5 kcal/mol, it has been demonstrated by experiments that hydrogen molecules squeezed into ice under GPa pressure remained locked inside ice lattice when the external pressure was withdrawn. [17,18] Even at GPa pressure, the hydrogen bonded ice lattice could stand up to the the van der Waals repulsion exerted by hydrogen molecules. The relative weakness of the hydrogen bonds, compared to typical chemical bonds, is actually a big advantage when it comes to the release of hydrogen through an aqueous valve. Moderate heating above the melting point easily disrupts the hydrogen bonds and opens the valves. Furthermore, such heating does not damage the dangling groups, and aqueous valves can be formed again upon exposure to water at lower temperatures.

For this study, a molecular model is built as shown in Figure 1a. Two types of singled walled carbon nanotubes, with an index of (12,12) or (15,15) respectively, are studied. Each tube is capped at one end and functionalized by carboxyl groups (-COOH) on the other end. The structure shall be labeled as (12,12)-COOH (with 24 carboxyl groups) and (15,15)-

COOH (with 30 carboxyl groups).

Aggregation of water molecules around the carboxyl groups is readily observed in the following simulation. Initially, a chunk of regular ice of Ih lattice, containing 640 water molecules, is placed 8 Å below the carboxyl groups, as shown in Figure 1b. During an MD simulation of 10 ns at 220 K, the ice chunk is melted and the water molecules are self-assembled around the hydrophilic carboxyl groups. The temperature is then gradually lowered from 220 K to 77 K over 1 ns, and an amorphous structure of water aggregates is formed at the end section, as shown in Figure 1c, which blocks the entrance into the tube and could potentially be an aqueous valve. Such a self-assembly process is facilitated when water is in its liquid state, and the simulation temperature of 220 K is above the melting point of water as described by the SPC/E potential, which is around 215 K. [19]

It is known from the phase diagram of ice [20] that its melting point changes little with pressure. The triple point for ice V, ice VI, and liquid water is identified at 0.63 GPa and 273 K. It means that in experiment hydrogen gas could be pressed to 0.63 GPa just above 273 K to fill open nanotube containers, and exposure to water, which is in liquid state under such conditions, could then induce self-assembly around the end section to seal off these containers. Such a scheme could also work at higher pressure, to ~ 1 GPa, when the temperature is raised to ~ 300 K, according to the experimental phase diagram.

For such a filling process, one must ask whether the formation of an aqueous valve is affected by the presence of hydrogen under high pressure. To simulate it, two artificial plates are introduced outside the tube, as shown in Figure 2a. Space between the two plates are filled by hydrogen molecules. By placing the bottom plate at different positions, the pressure of hydrogen could be raised to GPa range. Again, a chunk of ice is placed below the carboxyl groups, leaving the end section open for the filling of hydrogen inside the tube.

In the beginning step, water molecules in the ice chunk are artificially frozen in their positions, as hydrogen molecules are introduced between the plates at 250 K, which diffuse not only into the tube but also into the lattice of the fixed ice chunk, eventually reaching an equilibrium pressure of 0.6 GPa in 300 ps. Then the frozen water molecules are set free, and the temperature is raised to 270 K, so that the ice chunk is melted and the self-assembly of water molecules around the hydrophilic carboxyl groups is started. After 300 ps, an

aqueous valve is again formed. The system is then cooled down to 77 K in 500 ps, and the process produces the same kind of aqueous valve as shown in Figure 1, obtained in the absence of hydrogen. Careful examination of the structure shows that no hydrogen molecule is left inside the water aggregate. The result is not surprising because the non-polar and hydrophobic hydrogen molecules do not mix with the polar water molecules, and with their weak van der Waals potentials, hydrogen molecules can easily move out of the way of the aggregating water molecules. Finally, the two plates and the hydrogen molecules outside the sealed container are withdrawn, as in Figure 2b, and the system is equilibrated at 77 K for 300 ps. The aqueous valve is stable and no leakage of hydrogen molecules from inside the tube, which is at 0.6 GPa, is observed during the simulation.

While the above simulations prove that the container could be sealed off, with and without the presence of high pressure hydrogen, the robustness of such an aqueous valve must be further examined by calculating the diffusion barriers. A number of calculations are carried out in which a hydrogen molecule is forced to move through an aqueous valve by constraining the z coordinate of one particular hydrogen molecule, with z axis being the axial direction of the carbon nanotube. Typically, this hydrogen molecule would move close to the tube wall and find a path near the wall. As there is no hydrogen bond between the tube wall and water molecules, such a diffusion path produces less structural disruption.

Shown in Figure 3a is a typical potential energy curve along the diffusion path, when the internal pressure inside the tube and the external pressure outside the tube are both at zero. The z coordinate is chosen so that the averaged z coordinate for the C=O oxygen atoms in the -COOH groups around the end section is zero. In other words, $z = 0$ could be treated as an approximate dividing line, so that a hydrogen molecule is inside the container at positive z and outside the container at negative z values. The energy at $z = 10$ Å (inside the tube) is ~ 0.1 eV lower than the energy at $z = -20$ Å (outside the tube), since a hydrogen molecule inside the tube has more favorable van der Waals interactions with carbon atoms on the tube wall and other hydrogen molecules than its interaction with water molecules at an interstitial site of ice.

There are many barriers and wells connecting these two points along the potential energy curve. Starting from $z = 10$ Å, when the hydrogen moves into the aqueous valve, it

passes through two interstitial sites, seen as two energy minima (around $z = 1$ and $z = 4$ Å respectively), and hits a barrier of 1.0 eV centered near $z = 0$, where the carboxyl groups are located. Inside the tube, the diffusing hydrogen passes through the space between water and the nanotube wall. Near the end of the tube, the hydrogen molecule must squeeze through the spaces around the carboxyl groups covalently bonded to the nanotube, which accounts for the big barrier. The energy difference between the top of this peak and the position inside the tube is defined as the release barrier. Afterwards, the hydrogen moves into the outer part of the aqueous valve, which is mainly amorphous ice. There are several barriers in this region, which are more or less comparable to the diffusion barrier in Ih ice (~ 0.3 eV), although it could bump into a larger barrier too (e.g. at -12 Å), which is due to the disorder in the ice structure. There are of course many possible trajectories, and shown in Figure 3a is only a typical path. Molecular vibrations among the water molecules, carboxyl groups, and carbon nanotubes would produce further fluctuation in such paths. For each set of external and internal pressure, we have optimized eight diffusion paths and obtained average release barrier, listed in Table 1.

For (12,12)-COOH, the average release barrier decreases only slightly as the internal pressure is raised from 0 to 2 GPa. These values around 0.8 eV are significantly higher than the diffusion barrier through Ih ice (~ 0.3 eV), indicating that hydrogen can be held up inside the tube. The slight decrease in the release barrier is in agreement with the observation that the increase in internal pressure only induces small changes in the radial distribution function (RDF) of water molecules, shown in Figure 3b and 3c. When both P_{ext} and P_{int} are at zero, the RDF around the -COOH groups at the end section and the RDF in the amorphous ice outside the container are almost identical, with a sharp peak around 2.64 Å and a broad feature centered just above 4 Å. When the internal pressure P_{int} is increased to 1 GPa and the external pressure maintained at 0, the broad feature centered around 4 Å is maintained with its center slightly shifted to shorter distance for the RDF around the -COOH groups. For the ice outside the tube, the RDF is little changed. In other words, there is only slight structural tightening around the -COOH groups and little effect on the ice outside of the tube, when P_{int} is raised to 1 GPa, as the effect of the internal pressure is restricted by the tube wall and the valve.

The release barriers for the (15,15)-COOH valve are also calculated, as listed in Table 1, and the values are typically lower than the corresponding values for the (12,12)-COOH valve. More significant changes in the release barrier are also observed when the pressure is varied. With P_{ext} kept at zero, there is still a substantial barrier above 0.6 eV for the release of hydrogen, when P_{int} is at 0 or 1 GPa. However, when P_{int} is raised further to 2.0 GPa, the barrier drops to around 0.3 eV, which is comparable to the calculated diffusion barrier in ice. It indicates the difficulty for the (15,15)-COOH valve to hold hydrogen at an internal pressure of 2 GPa. Such differences between the (15,15)-COOH and (12,12)-COOH valves are due to the difference in their diameters, 20.3 Å for the former, and 16.3 Å for the latter, respectively. For the larger (15,15)-COOH valve, the end section is not completely dominated by the -COOH groups at the edge and their hydrogen bond interactions with the water molecules, because there is a chunk of ice around the center of the section. It makes the valve more flexible as a hydrogen molecule squeeze through the valve, which accounts for reduced barriers for hydrogen diffusion. One could project that as the tube diameter increases further, the influence exerted by the -COOH groups will be limited only to the edge of the valve, and most part of the valve is just a chunk of ice. To seal off such tubes for hydrogen storage, the length of the hydrophilic groups should be extended, to tighten their hold around the water aggregate.

The carboxyl groups, on which an aqueous valve is assembled, contain C=O, C-O and O-H bonds, which are robust covalent bonds little affected by the pressure of a few GPa. The van der Waals repulsions only slightly decrease the average bond distances, by ~ 0.001 Å for the C-O bond and ~ 0.0001 Å for C=O bond, when the internal and external pressures are raised from 0 to 2 GPa.

The weak structural link in our model aqueous valve is the hydrogen bonds that hold the water aggregate to the carboxyl groups. The energy for such a typical hydrogen bond is only 5 kcal/mol, and at high internal pressure, the force exerted on the valve may be strong enough to break collectively these hydrogen bonds and push the water aggregate out of the tube. The threshold pressure can be evaluated by molecular dynamics simulations. Hydrogen molecules are added consecutively inside a sealed container step by step. At each step, the configuration is first optimized at 0 K, and then the temperature is gradually

raised to 77 K and equilibrated for 100 ps. The threshold pressure is found to be 3.0 GPa for (12,12)-COOH and 2.6 GPa for (15,15)-COOH respectively, when the aqueous valve is pushed out during the equilibration step

The storage pressure envisioned for aqueous valves is between 0.6 GPa around 273 K and 1.0 GPa around 300 K, for which the mechanical stability is not a concern. These two pressures are determined by the phase diagram of water. To seal off the valve, water should be in liquid state to facilitate its self-assembly around the tube ends. Using the equation of state measured by Mills and co-workers, [21] the molar volume of hydrogen is 17.1693 cm³ at 0.6 GPa and 273 K, and 14.6072 cm³ at 1.0 GPa and 300 K, both being more favorable than even the molar volume around 23 cm³ for solid hydrogen at 4.2 K. [10]

The weight storage efficiency varies with the tube diameter. With the carbon atoms on the tube surface, the efficiency is higher for tubes with larger diameters since they have larger volume to surface ratios. For a long tube, the weight of the aqueous valve adds only a very small overhead and could be ignored, and the H/C mass ratio α can be estimated by the weight of hydrogen contained in the volume of a tube segment and the weight of carbon on the tube wall (see supporting information), which is

$$\alpha = \frac{3d_{CC}\pi\rho}{48n}\left(\frac{1.23n}{\pi} - d_{CH}\right)^2$$

for an (n,0) tube, and

$$\alpha = \frac{\sqrt{3}d_{CC}\pi\rho}{48n}\left(\frac{1.23\sqrt{3}n}{\pi} - d_{CH}\right)^2$$

for an (n,n) tube. In the above formula, d_{CC} is the C–C distance on a carbon nanotube, taken to be 1.42 Å, ρ is the hydrogen mass density in a.m.u/Å³, and d_{CH} is the shortest distance between the surface of a spherical hydrogen molecule and a carbon atom on a carbon nanotube for the calculation of available storage volume, which is taken as 1.6 Å based on previous studies. [22] At 0.6 GPa and 273 K, the calculated weight efficiency, which is plotted in Figure 4, reaches 5% at a tube diameter of 2.0 nm and 8% at 3.0 nm. At 1 GPa and 300 K, the weight efficiency reaches 5% at 1.8 nm, and close to 10% around 3.0 nm.

In principle, an aqueous valve could be built for larger tubes by extending the -COOH groups around the tube edge in our model to longer polymeric and hydrophilic chains

so that they could be extended to the central portion of the valve. The melting point of an aqueous valve is another important consideration. While the storage of high pressure hydrogen inside the tube requires the aqueous valve to be in the solid state, the release of the hydrogen is achieved by the melting of the aqueous valve. It should be noted that many opportunities exist in modifying the functional groups to produce various structures for the aqueous valve and to adjust its melting point. In synthetic chemistry, the oxygen containing groups can be easily transformed. The length, ionic strength and branching can be controlled by introducing groups that bound more strongly with water molecules, such as polycarbonate, polysilicate, or polyphosphate groups. The change in the pH value or the presence of salts could also affect strength of the binding of these groups to water. These aspects of the valve design are currently being investigated in our groups.

In summary, we have demonstrated by molecular dynamics simulation that the oxygen containing dangling groups around the edge of an opened carbon nanotube could serve as the frame for the self-assembly of water molecules to produce an aqueous valve. Formation of such an aqueous valve is also demonstrated in the presence of high pressure H_2 . Using a (12,12) tube and a (15,15) tube with $-COOH$ groups as models, substantial diffusion barriers are identified, for storage pressure in the 1-2 GPa range. They provide the basis for a new design of high pressure nano-containers for the storage of hydrogen that could be implemented and tested in experiments.

Computational Details:

Molecular dynamics simulations are performed by the TINKER 4.2 package. [23] The equation of motion is solved by the Beeman algorithm with time step of 1 fs [24] and the system temperature is controlled by a Nosé-Hoover thermostat. [25,26] The OPLS-all-atom field with L-J potentials is applied to the carbon atoms on CNT and to the carboxyl groups. For water molecules, SPC/E model is employed. A hydrogen molecule is treated as spherical and the interactions between two hydrogen molecules are modeled by the Silvera-Goldman potential. [10,27] The interaction between hydrogen and water molecules is L-J potential. [28] Our calculated barriers for type-sII clathrate are in good agreement with the previously reported values. [29] Within Ih ice, the diffusion barrier of a hydrogen molecule is found to be

0.3 eV along a/b direction and 0.2 eV along c direction, which is also reproduced by simulations using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) program. [30] The interactions between carbon atoms are modeled by the second-generation reactive empirical bond order potential. [31] The van der Waals interaction between a hydrogen molecule and a carbon atom is described by the recently fitted potential by some of us, which reproduces the high level *ab initio* results over a wide range of attractive and repulsive regions. [32] The cutoff for all unbonded interactions is set to 60 Å. For different types of atoms, the L-J potential is calculated by the Lorentz-Berthlot combination rules. Four carbon atoms on the carbon nanotube are fixed to prevent unnecessary movement of the tube during all the simulations.

Acknowledgement:

This research is supported by the Research Grant Council of Hong Kong through Project 402309. Supports from Natural Science Foundation of China, National Basic Research Program of China (973), Shuguang and Innovation Program of Shanghai Education Committee are acknowledged. The computation is performed at the Supercomputer Center of Shanghai and ECNU.

References

- [1] M. Monthieux, Carbon **40**, 1809 (2002).
- [2] J. Sloan, A. I. Kirkland, J. L. Hutchison, and M. H. Green, Acc. Chem. Res. **35**, 1054 (2002).
- [3] A. N. Khlobystov, D. A. Britz, and G. A. D. Briggs, Acc. Chem. Res. **38**, 901 (2005).
- [4] X. Ye, X. Gu, X. G. Gong, T. K. M. Shing, and Z. F. Liu, Carbon **45**, 315 (2007).
- [5] O. V. Pupysheva, A. A. Farajian, and B. I. Yakobson, Nano Lett. **8**, 767 (2008).
- [6] D. Y. Sun, H. Y. Chen, J. W. Liu, X. G. Gong, and Z. F. Liu, Phys. Rev. B **79**, 033403 (2009).

- [7] H. Y. Chen, X. G. Gong, Z. F. Liu, and D. Y. Sun, *J. Phys. Chem. C* **115**, 4721 (2011).
- [8] H. Y. Chen, Z. F. Liu, X. G. Gong, and D. Y. Sun, *Microfluidics and Nanofluidics* **10**, 927 (2011).
- [9] M. V. Suyetin and A. V. Vakhrushev, *J. Phys. Chem. C* **115**, 5485 (2011).
- [10] I. F. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).
- [11] R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **61**, 857 (1988).
- [12] L. Sun, F. Banhart, A. V. Krashennnikov, J. A. Rodriguez-Manzo, M. Terrones, and P. M. Ajayan, *Science* **312**, 1199 (2006).
- [13] A. V. Vakhrushev and M. V. Suyetin, *Nanotechnology* **20**, 125602 (2009).
- [14] B. I. Yakobson, *Physica Scripta* **36**, 513 (1987).
- [15] A. Kuznetsova, I. Popova, J. T. Yates Jr., M. J. Bronikowski, C. B. Huffman, J. Liu, R. E. Smalley, H. H. Hwu, and J. G. Chen, *J. Am. Chem. Soc.* **123**, 10699 (2001).
- [16] A. Kuznetsova, D. B. Mawhinney, V. Naumenko, J. T. Yates Jr., and R. E. Liu, J. Smalley, *Chem. Phys. Lett.* **321**, 292 (2000).
- [17] V. V. Struzhkin, B. Militzer, W. L. Mao, H. K. Mao, and R. J. Hemley, *Chem. Rev.* **107**, 4133 (2007).
- [18] W. L. Mao, H. K. Mao, Y. Meng, P. J. Eng, M. Y. Hu, P. Chow, Y. Q. Cai, J. F. Shu, and R. J. Hemley, *Science* **314**, 636 (2006).
- [19] A. Alexiadis and S. Kassinos, *Chem. Rev.* **108**, 5014 (2008).
- [20] V. F. Petrenko and R. W. Whitworth, editors, Oxford University Press, Oxford, 2002.
- [21] R. L. Mills, D. H. Liebenberg, J. C. Bronson, and L. C. Schmidt, *J. Chem. Phys.* **66**, 3076 (1977).
- [22] Q. Y. Wang and J. K. Johnson, *J. Chem. Phys.* **110**, 577 (1999).

- [23] J. W. Ponder and F. M. Richards, *J. Comp. Chem.* **8**, 1016 (1987).
- [24] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, U.K., 1993.
- [25] S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
- [26] W. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- [27] I. F. Silvera and V. V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978).
- [28] S. Alavi, J. A. Ripmeester, and D. D. Klug, *J. Chem. Phys.* **123**, 024507 (2005).
- [29] T. J. Frankcombe and G. J. Kroes, *J. Phys. Chem. C* **111**, 13044 (2007).
- [30] S. Plimpton, *J. Comp. Phys.* **117**, 1 (1995).
- [31] D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, *J. Phys.-Cond. Matt.* **14**, 783 (2002).
- [32] D. Y. Sun, J. W. Liu, X. G. Gong, and Z. F. Liu, *Phys. Rev. B* **75**, 075424 (2007).

Table 1: $E_{release}$, the barriers for a hydrogen molecule to diffuse through an aqueous valve, for various internal pressure P_{int} and external pressure P_{ext} .

System	$P_{ext}(GPa)$	$P_{int}(GPa)$	$E_{release}(eV)$
(12, 12) – <i>COOH</i>	0	0	0.85±0.23
	0	1	0.79±0.16
	0	2	0.81±0.16
	2	0	1.08±0.30
	2	2	0.95±0.07
(15, 15) – <i>COOH</i>	0	0	0.67±0.17
	0	1	0.64±0.20
	0	2	0.32±0.08
	2	0	0.91±0.11
	2	2	0.80±0.17

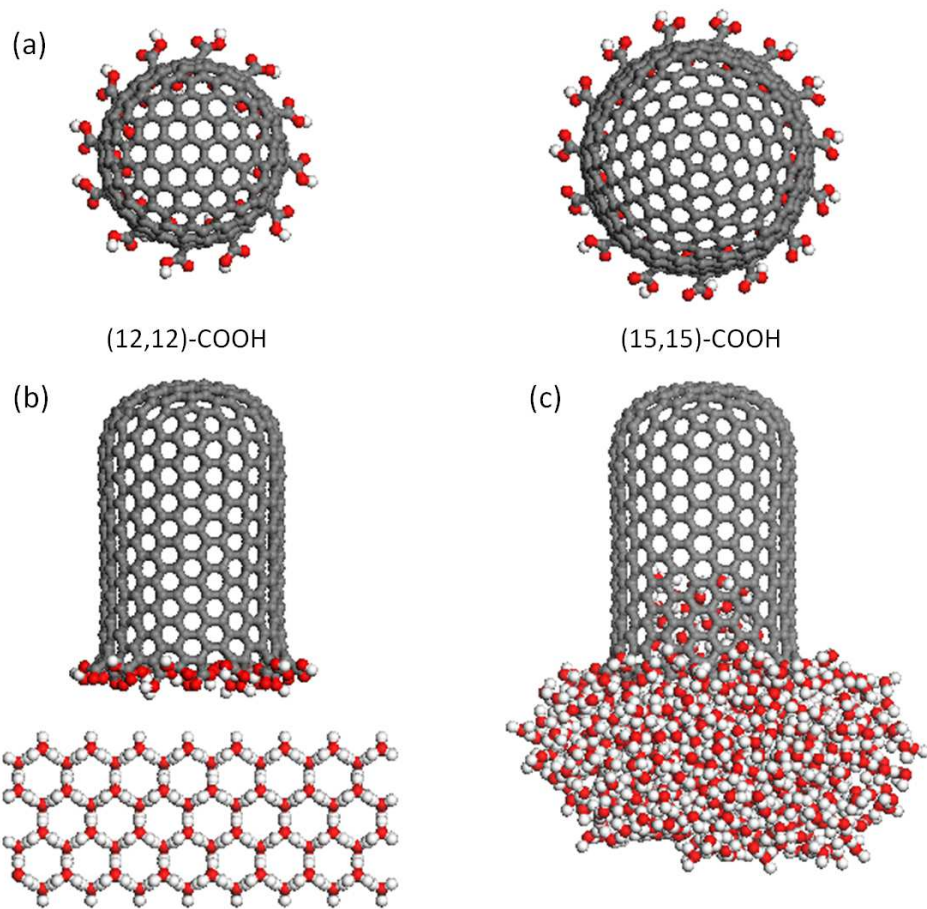


Figure 1: Formation of an aqueous valve in the absence of hydrogen. (a) Top view of valve (12,12)-COOH and (15,15)-COOH; (b) A nano-container separated from a chunk of ice, as the initial configuration for MD simulation; (c) Melting of the ice chunk leads to the self-assembly of water molecules around the end -COOH groups.

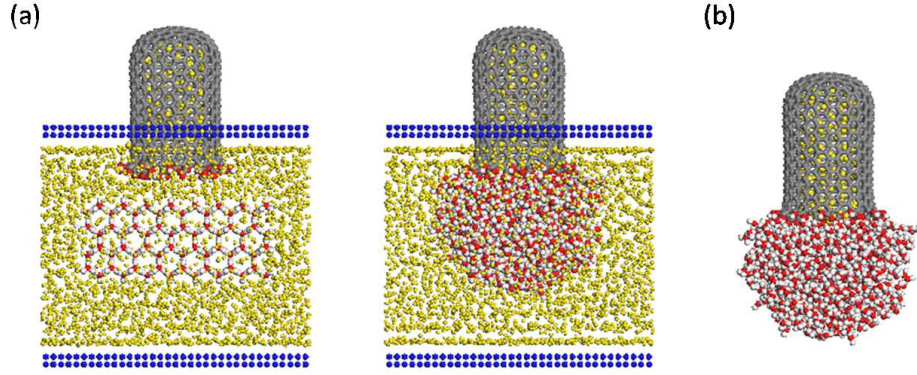


Figure 2: Formation of an aqueous valve in the presence of hydrogen with a pressure of 0.6 GPa which is controlled by two slabs (in blue). (a) In the initial structure, the ice chunk is again frozen, while hydrogen molecules (yellow particles) of 0.6 GPa fill the container and the ice lattice. After melting of the ice chunk, water molecules again self-assemble around the -COOH groups to form an aqueous valve. (b) After the withdrawal of external hydrogen, the aqueous valve is stable. It demonstrates a filling procedure in which the hydrogen is filled into open container in high pressure and afterwards the container is sealed off by exposure to liquid water.

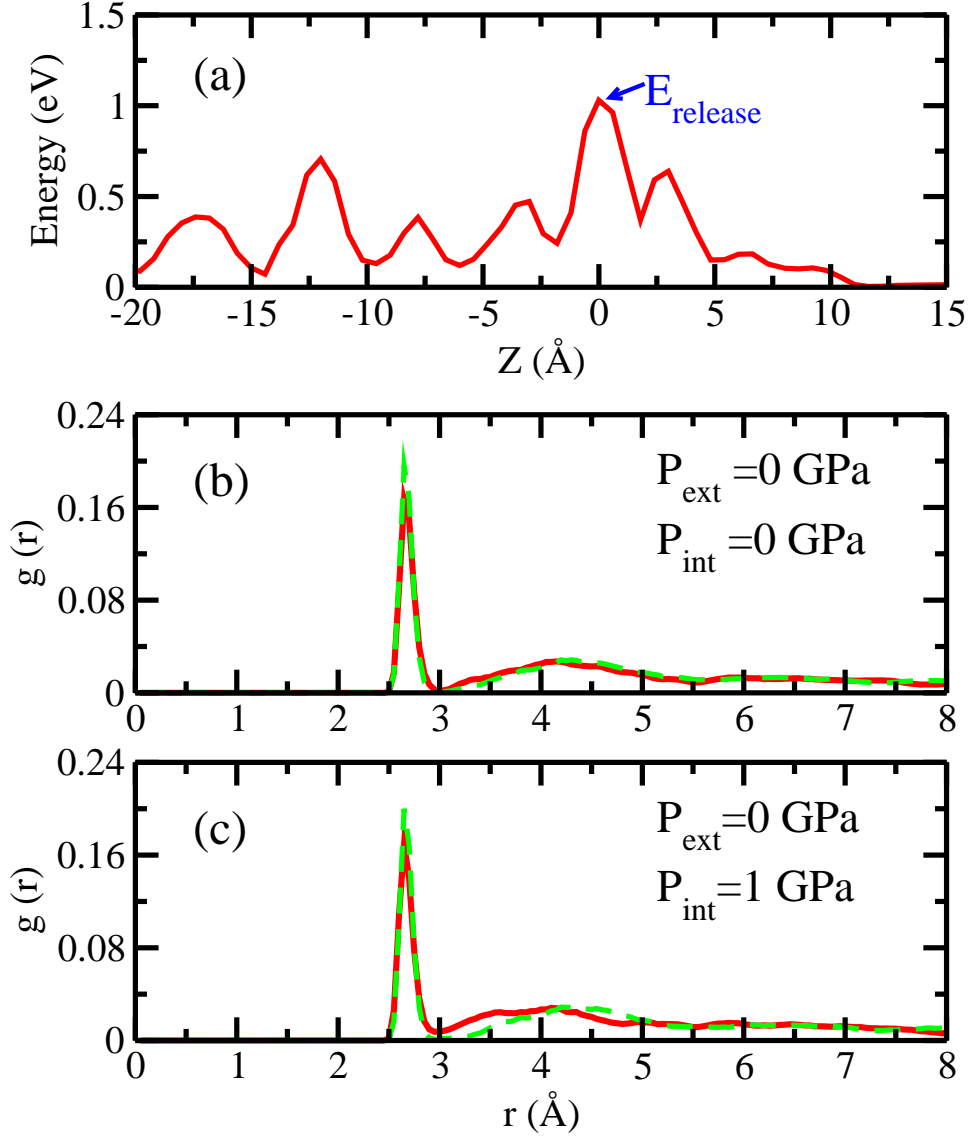


Figure 3: (a) A typical potential energy curve as a hydrogen molecule diffuses through the valve. (b) Radial distribution function $g(r)$ for O-O in water close to (red)/far from (green) the carboxylic groups for $P_{\text{ext}}=0$ and $P_{\text{int}}=0$ GPa. (c) $g(r)$ for O-O for $P_{\text{ext}}=0$ and $P_{\text{int}}=1$ GPa.

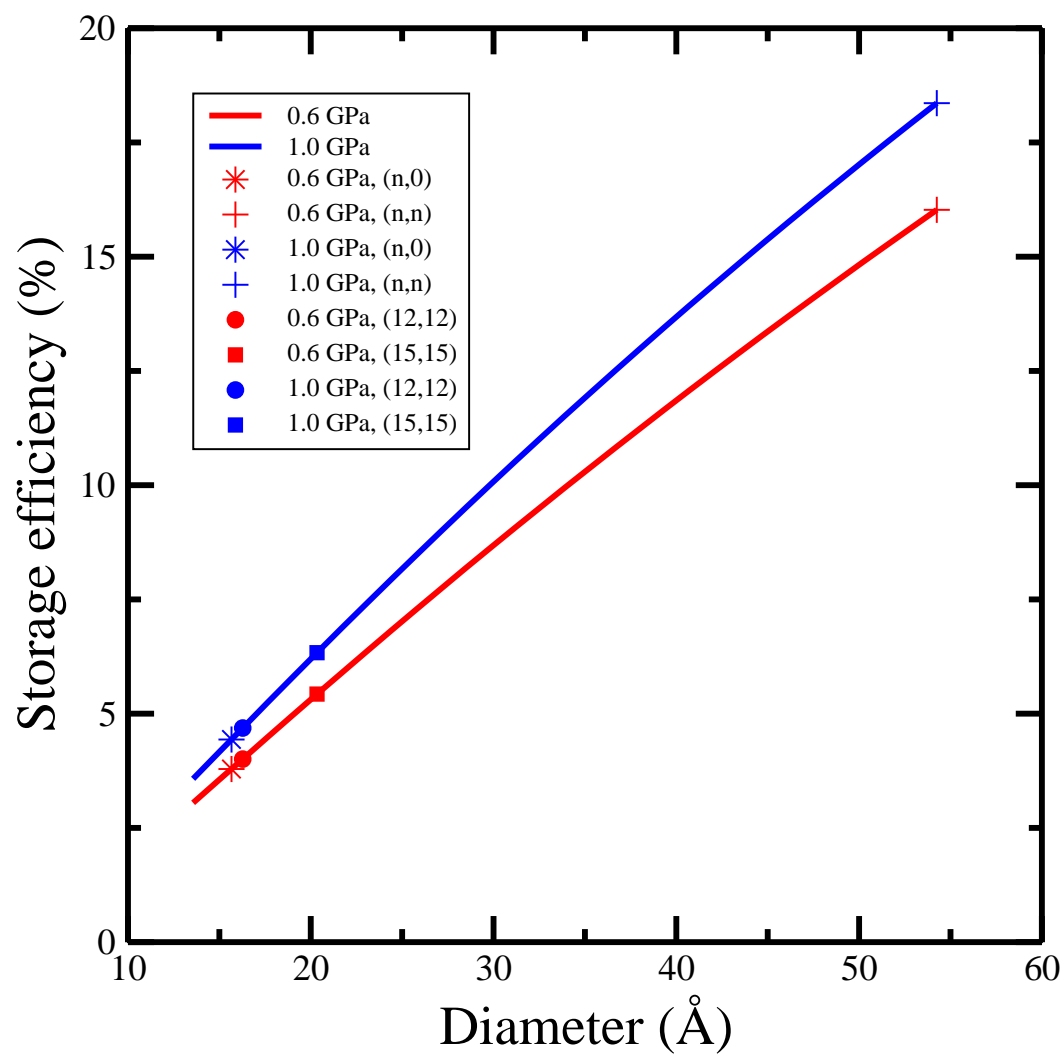


Figure 4: Calculated weight efficiency curve as a function of tube diameter, under two conditions, 0.6 GPa/273 K, and 1.0 GPa/300K.